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CORRECTION

Manuscript titled "Effect of pitch preparation on its colloidal properties and deposition behaviour"
by K Stack, R Lee, R Rao, D Richardson, G Garnier and T Lewis

published on Page 273 of the proceedings was inadvertently included in place of the correct manuscript

"Measurement of pitch deposition by impinging jet microscopy: Effect of divalent salts"
by
Roland Lee, Karen Stack, Trevor Lewis, Gil Garnier, Des Richardson and Theo Van de Van

Measurement of pitch deposition by impinging jet microscopy: Effect of divalent salts.

ROLAND LEE[1], KAREN STACK[1], TREVOR LEWIS[1], GIL GARNIER[2], DES RICHARDSON[3], THEO VAN DE VAN[4]
[1] University of Tasmania,
[2] Monash University,
[3] Norske-Skog, Boyer, Tas Australia
[4]McGill University,Montreal, Canada.

Abstract
Papermakers for many years have had to contend with the wood resins that are released during pulping and papermaking. As paper mills reduce water consumption by further process loop closure, there is potential for the problems to increase. Accumulated organic and inorganic material can lead to deposits on machinery, poor process control, loss in efficiency, and lower product quality. There are a number of factors, which have an impact on the deposition tendencies of colloidal particles as a result of different inorganic materials or salts. Along with the valency of the salt, the concentration of salt, the properties of the colloidal particles, and the chemical nature of the surface are important. Variations in colloidal stability and deposition are observed even for salts of the same valency.

With the use of impinging jet microscopy (IJM) the deposition of pitch on to hydrophobic and hydrophilic model surfaces was measured and the effect on the rate of deposition was quantified with changing cation. On both model surfaces the pitch deposition was seen to be slightly faster when calcium at 800 mg/L was present than magnesium at the same concentration. This concentration is around twice the critical coagulation concentration. The concentration of calcium in process water in some paper mills can be 200 – 300 mg/L. With further process loop closure this could rise to levels being investigated in this study. The concentration of magnesium would normally be much lower than this unless magnesium based alkalis were to be used.

The rate of deposition onto the model hydrophobic surface was far greater (up to a 2.5 times) than on the hydrophilic surface for both salts. Contact angle measurements inferred that in the air-surface environment the hydrophobicity of the surface doesn't affect its affinity for neat pitch suggesting that the pitch may be reforming on the surface. IJM results show variation in the pitch shape on the model surfaces. It is possible that molecular reorganization of the components occurs at the surface and water interfaces. On the hydrophilic surface the pitch particle size for both salts is about 0.33-0.35 μm while for the hydrophobic surface the particle size is about 5 times more for the calcium salt than the magnesium salt. Film thinning or spreading of the pitch particles was observed to occur on the hydrophobic surface with calcium and to a lesser extent with magnesium salt. With time film thinning will affect the chemistry expressed by the surface and change the interaction of other process components in the paper making process.

Introduction
Significant volumes of water are used in the pulp and paper industry in the pulping of wood chips and formation of the paper. World's best practice for water consumption in manufacture of mechanical paper grades is around $14m^3$ $tonne^{-1}$ of product *(1)*. The most water efficient of Norske Skog's mills operates at around 9 m^3 $tonne^{-1}$, but climatic conditions can be such that even further reductions would be welcome. Further closure of the process water loop however would lead to an increase in the amount of organic and inorganic material recycled in the process. The accumulated organic and inorganic material can lead to deposits on machinery, poor process control, loss in efficiency, and lower product quality.

The organic material includes compounds like resin acids, fatty acids, and fatty acid esters, known collectively as "wood resins" or "pitch" These constitute a very complex mixture, making the prediction of how they react with other system components difficult *(2-9)*. Inorganic ions such as calcium or aluminium react with the soluble resin acids to form sticky deposits of metal soaps that are not seen on the addition of magnesium and sodium *(6, 7, 9-14)*.

Previous work has focused on investigation of changes to the concentrations of wood resins in the sample, along with changes in the salt concentrations and salt type *(9, 15-17)*. Recent work using a photometric dispersion analyzer (PDA) has shown variation in the rate of aggregation of the wood resins is dependent on the salt present, for example growth of pitch particles is faster in the presence of magnesium salts compared to calcium salts *(18)*.

For particle-surface interactions there are a number of key factors involved in deposition including hydrodynamic conditions in the region of the surface, and particle transport, adsorption and adhesion. Direct quantitative measurement of the deposition rate is made possible with the use of the impinging jet microscopy (IJM) and video imaging. IJM gives quantitative information of particles absorbed onto

the surface with well-defined hydrodynamic and physical-chemical properties *(19)*.

Figure 1 shows the schematic view of the impinging jet consisting of two plates (collector plate and bottom confiner plate) where r is the radius of the jet h is the distance between the plates and particle counts were collected at the Stagnation point. Within the impinging jet the flow of particles forms a Newtonian flow *(20-23)*. This enters through a circular hole impinging onto the collector plate. The rate of deposition and flow distribution is defined by the dimensionless ratio of h/r. The experimental rate of deposition (j) is defined as the number of particles on the surface (n_s) with time (t):

$j = n_s / t$

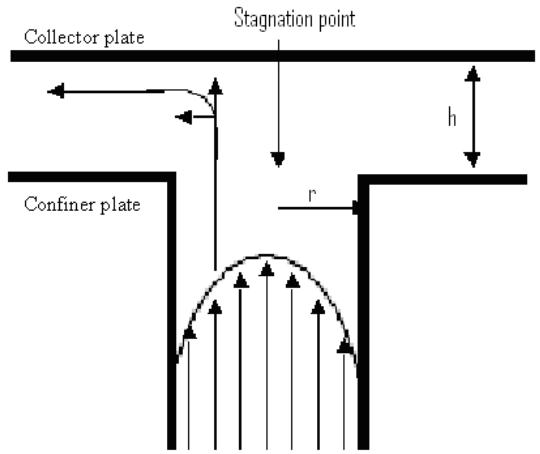

Figure 1: Schematic view of a radial impinging jet.

A solid substrate when placed in contact with solvent rich environment will be covered in a thin film of fluid. The technique allows the observation of only those particles that are absorbed to the surface.

The technique has been used to probe numerous deposition problems including the competitive deposition of PEI coated particles and absorption of PEI to a surface *(22)*. The kinetics of adhesion for phosphatidylcholine liposomes to quartz surfaces *(23)* and the deposition of particles onto cellulose films *(24)* have also been studied using impinging jet.

The nature of both the surface and chemical composition of the material interacting with the surface are important. Qin et al showed that when a droplet of water was introduced to a surface coated with pitch components the pitch contact angle and wettablity is dependant on its chemical composition and the surface *(15-17)*.

In this paper the direct measurement of the deposition of colloidal pitch particles on different substrates has been conducted with the use of impinging jet microscopy. This enables the effect of different salts on the pitch "stickiness" and the effect of the surface physiochemical characteristics on the rate of deposition to be studied.

Methods

Pitch Preparation

A thermomechanical pulp (TMP) made from *Pinus Radiata* was collected from the primary refiners at Norske Skog, Boyer, Tasmania. The pulp was air-dried and soxhlet extracted for 8 hours with hexane.

Aqueous wood resin dispersions of 100 mg/L concentration were prepared by the addition of dissolved extracted wood resin in acetone (99.5% purity, Sigma-Aldrich) to a 1 mM KNO_3 solution in distilled water with a pH of 5.5. Dialysis of the dispersion was performed using cellulose membrane tubing with a molecular mass cut off of 12,000 amu (Sigma-Aldrich D9402-100FT), to remove acetone. The wash water used was 1 mM KNO_3 pH adjusted to 5.5. This was changed every hour for the first 5 h and then at 24 h.

All electrolytes used were dissolved in distilled water. Constant volumes were added to the impinging jet sample solution, such that the final volume had the required concentration of salt. $CaCl_2$ and KNO_3 were purchased from BDH (99.8 purity %). $MgCl_2$ (99.8% purity) was obtained from Merck.

Hydrophobic conversion of glass slides

Microscope glass slides (CANEMCO & MARIVAC Frosted End Microscope Slides 75 x 25 mm) where immersed in a 50/50 solution of trimethylchlorosilane and pyridine (≥99% Sigma- Aldrich) at 60°C for 12 h, removed and cleaned with hexane (99.8% Sigma-Aldrich) and air dried.

Contact angle measurements

The contact angle measurements were conducted with the use of a Data Physics OCA 20. A 10 µL drop of water was placed on the surface and the contact angle assessed with SCA20 software. This procedure was the same for the contact angle of pitch with the model surfaces. A 100 µL drop of pure extracted pitch, prior to formation of the pitch colloids, was introduced to the model surfaces and the contact angle of the pitch on the surface was determined.

Impinging jet

The dialysed pitch colloidal dispersion was made up to salt concentration of 20 mM with the desired salt and stirred for 10 min to allow particles to aggregate. The h/r ratio within the jet was kept at 1.7 for all experiments, with a constant flow rate of 70 mL/min through the impinging jet.
Magnification of 10 times objective was achieved with an Autoplan microscope. Images were captured with the use of an IMI tech Han series digital camera.

Results
Contact angle measurements for the model hydrophilic and hydrophobic surfaces with water and pitch were made. Figure 2 depicts the contact of water with untreated glass slide with a contact angle calculated to be 18^{o}. This shows a high affinity between the surface and the water confirming that the surface is hydrophilic.

Figure 2: Water contact angle with model hydrophilic surface (18 °).

In contrast to this in figure 3 the contact angle post silylation of the surface with trymethylchlorosilane and water is 118°. This indicates that the model surface is hydrophobic and so can be used to model similar surfaces found in a real system.

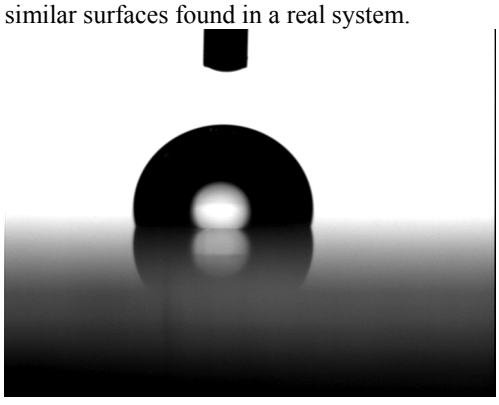

Figure 3: Water contact angle with model hydrophobic surface (118 °).

Droplets of neat wood resin were placed onto the model surfaces in an air environment as shown in figure 4 with a contact angle of 18° for both surfaces. It is apparent from the contact angle measurements that the surface has little or no effect on the contact angle of pitch in the absence of water.

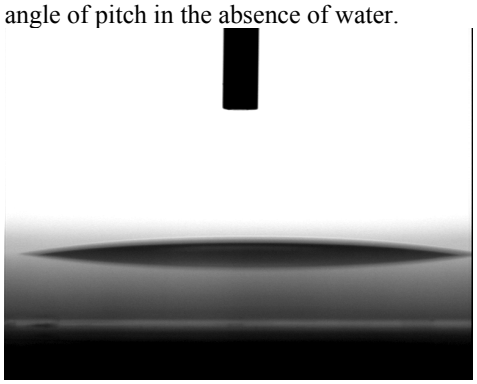

Figure 4: Wood resin contact angle with model hydrophobic surface (18°).

The rate of deposition onto the two surfaces was assessed by counting the total number of particles on the surface at various times. Figures 5 and 6 show the typical droplet formation of particles of pitch from 20 mM of $MgCl_2$ and 20 mM $CaCl_2$ respectively onto a hydrophilic collector plate.

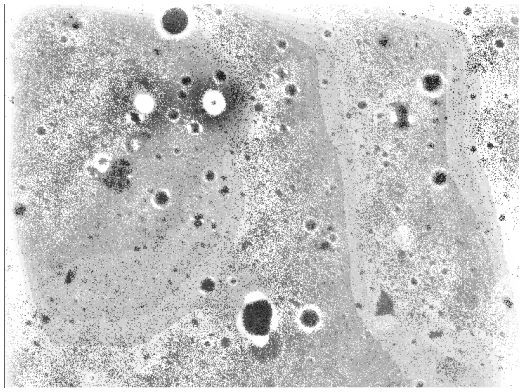

Figure 5: Pitch deposition onto a model hydrophilic surface with $MgCl_2$.

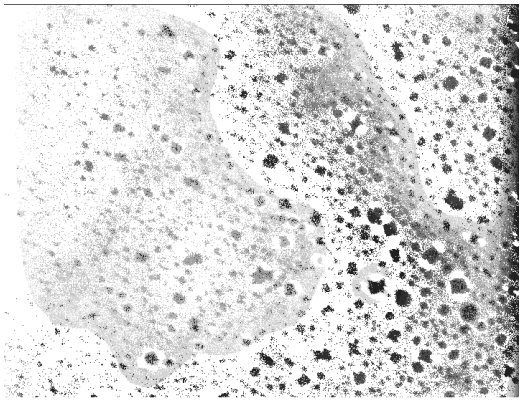

Figure 6: Pitch deposition onto a model hydrophilic surface with $CaCl_2$.

For both salts the pitch was seen to form on the glass as a droplet. This droplet may be distinguished from the background via the ring encircling the particle from the reflection of light and the difference between the refractive indices of water and pitch.

In figure 7 the deposition of pitch onto a hydrophobic surface is shown. It can be seen from the absence of the "halo" around the particles that the droplet formation changes with the change of surface chemistry and the particles are no longer distinct droplets on the surface.

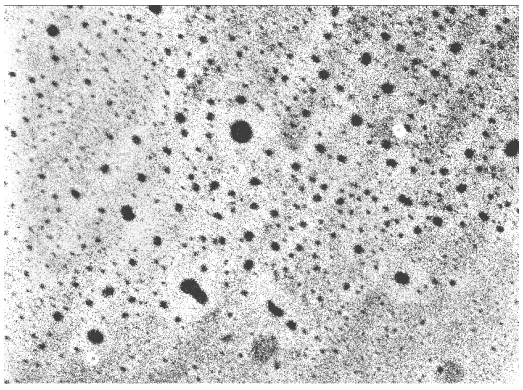

Figure 7: Pitch deposition onto model hydrophobic surface with $CaCl_2$.

Over a period of time the deposited pitch forms an oil film on the hydrophobic surface as seen in figure 8. This phenomenon is not seen with the model hydrophilic surface even over a prolonged period of time. The effect is known as film thinning. The oil film was found to obscure the rate of deposition. In order to overcome this effect, the surface was cleaned after each run and the zero time was taken as the time the pitch first contacted the cleaned surface.

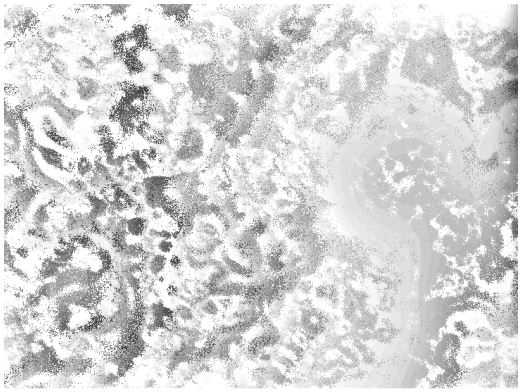

Figure 8: Pitch deposition onto a model hydrophobic surface with $CaCl_2$. after a period of time.

Figure 9 presents the average particle size of the pitch on the model surfaces after 60 sec of deposition. It can be seen that pitch particles on the hydrophilic surfaces are smaller than those on hydrophobic surfaces. Furthermore the large difference between the hydrophobic surfaces for the calcium and magnesium salts is related to the amount of film thinning or wetting of the surface that is experienced. More film thinning was observed with the calcium salt and as a result a larger particle size was measured with a larger amount of variation in the particle size as indicated by the error bars.

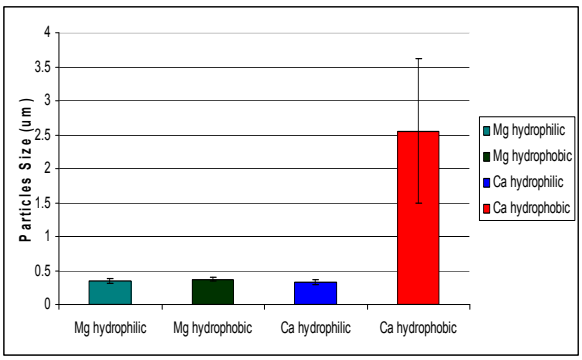

Figure 9: The average particle size for the deposited pitch after 60 sec of deposition onto the surface.

The particles were found to deposit faster on to the hydrophobic surfaces as shown in Figure 10. The rate of pitch deposition is equal to particles /second or the slope of the lines of best fit in figure 10. On the hydrophilic surface the pitch deposition rate in the presence of magnesium salt is 41 counts/sec and this increased to 103 counts/sec with the change in surface to a hydrophobic one. This indicates a 2.5 fold increase in the particle-surface interaction. In the presence of calcium salt, this increase in the affinity

of the pitch particles is also seen. However the change is not as marked, with a 1.8 fold increase.

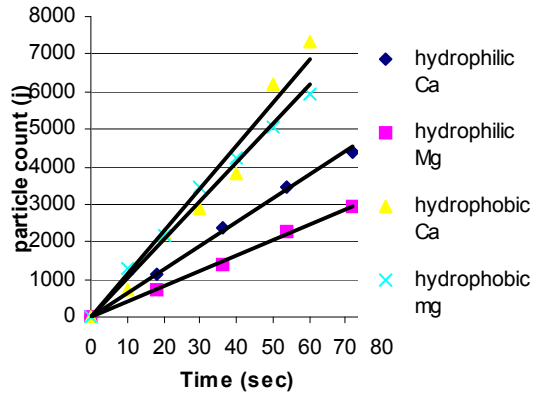

Figure 10: Flux of particles to the surface with different salt types ($CaCl_2$ and $MgCl_2$) and surface conditions (hydrophobic and hydrophilic).

Discussion

The wood resin dispersions being deposited onto the surfaces were at pH 5.5 which is below the resin acid and fatty acid pKa's. As such fatty acid and resin acid components in the wood resins will be mostly un-ionised. These acids contain a hydrophilic head group (the carboxylic acid) and a hydrophobic tail. The molecules can reorient themselves so that the polar group will interact with a hydrophilic surface or the non-polar groups can orientate and interact with the hydrophobic surface. The low contact angle observed for neat pitch on the two different surfaces (figure 4) can be explained by this ability of the molecules to reorient. However orientation of the component molecules of pitch in a water environment is restricted due to water-pitch interactions. This may then change the manner in which the pitch can deposit onto a surface in water and the form it will take.

The large size difference in the particles between the magnesium salts and the calcium salts on a hydrophobic surface and the differences in the amount of film thinning that occurred indicate that the pitch particles are interacting with the surface in different manners. It is possible that the small number of ionized resin components is reacting with the calcium metal salts in solution forming non-polar metal soaps. Due to the hydrophobicity of the core of the colloid and the mobility of components in the colloidal particles the metal resonates may move to the core of the particles. This change results in an increase in the concentration of non-polar component in the particle and the consumption of the resins. Further work is being undertaken to study this and determine if this does occur.

As all experiments are conducted above the critical coagulation concentration, the deposition of pitch will readily occur through compression of electrical double layer promoting aggregation and destabilization of the particles. Deposition is noted to occur on both surfaces (figures 6 and 7) however there is variation in the rate of deposition due to the change in surface polarity. This indicates that pitch will deposit onto both hydrophilic and hydrophobic surfaces but the wood resins have a higher affinity for the hydrophobic surface. Hydrophobic modification of the surface results in the reduction of the surface charge. As a result the electrical double layer associated with the surface is reduced, and hence the repulsive forces associated with it. The, interactions that have to be overcome for fast particle-surface interaction, will be proportionally reduced. The results indicates that the critical deposition concentration (CDC) for pitch onto the model hydrophilic surface is greater than the 20mM salt added to the wood resin solution., Further work is required to find the CDC's for pitch onto the model surfaces used.

The film thinning that occurred on the hydrophobic surface enables the pitch to conform easily to the surface as an oil coating. This will with time obscure further deposition of particles onto the model surface. It is possible that the more hydrophobic components of pitch migrate to the solid hydrophobic surface and the hydrophilic components to the pitch-water interface and so change the chemistry and nature of the surface solution interactions. Further work will be conducted to study this effect in more detail.

The salt concentration levels investigated in this study correspond to levels of 800 mg/L which are meant to represent mill conditions of increased water closure. Calcium concentrations of levels of 200-300mg/L are not uncommon in many mills and so the levels investigated are within levels that would occur with increased water closure. The results indicate that surfaces that are hydrophobic in nature within the paper machine will form oil films with higher deposition rates than on hydrophilic surfaces. The formation of the pitch oil film layer will then absorb the fibres and process material that comes into contact with it. This will result in the tacky deposits observed in the mill that contains a mixture of fibres and wood resins. Unless magnesium based process

additives were to be used, concentrations of magnesium will remain much lower than this.

Conclusion

In the air-surface environment the hydrophobicity of the surface doesn't affect its affinity for neat pitch. However, pitch in a water environment is more structured due to water-pitch interactions, as seen by the differences in appearance of the deposited pitch on the hydrophobic and hydrophilic surfaces in the IJM experiments.

On both model surfaces the pitch deposition was seen to be faster in the presence of calcium salt. The rate of deposition was 62 counts/sec for the hydrophilic surface and 115 counts/sec for the hydrophobic surface, a 1.8 fold increase in the rate of deposition.

A 2.5 fold increase in the interaction of pitch with the surface is noted from the rate of pitch deposition onto the hydrophobic surface compared to the hydrophilic surfaces in the presence of magnesium salt. Deposition onto the hydrophilic surface for magnesium is 41 counts/sec, increasing to 103 counts/sec with the change in surface to the hydrophobic model surface.

Over time, the formation of an oil film will change the nature of the surface solution interactions. It is inferred that surfaces that are hydrophobic in nature within the paper machine will form these oil films more readily then hydrophilic surfaces. The formation of these films will result in the tacky deposits observed in the mill that contains a mixture of fibres and wood resins.

Acknowledgments

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